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EXTRACTION OF SOME ELEMENTS WITH PHOSPHOROUS-CONTAINIG
MONOBASIC ACIDS

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A wide application of acidic phosphororganic compounds for
solvent extraction determines the interest for the extraction mechan-
ism and the structure dependence of the extraction power of these
reagents.

For the extractants considered the group $P\begin{smallmatrix}O\\OH\end{smallmatrix}$ is common in
which acidic hydrogen is substituted by cation,while phosphoryl
oxygen is capable of a coordination link with an element being
extracted.

The following schematic equations correspond to these mechanisms:

$$Me^{z+}+z(H_2R_2) \rightleftarrows Me(HR_2)_z+zH^+ \qquad (1)$$

$$Me^{z+}+zX + mS \rightleftarrows MX_z \cdot mS \qquad (2)$$
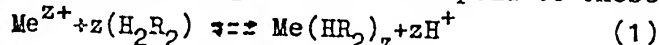
Despite numerous investigations into the extraction of various
elements with alkilphosphoric acids(1-20),there remain many aspects
of the extraction of mono-,bi- and polyvalent cations to study more
completely. While the extraction of slightly polarized elements may
be satisfactoril described in terms of the equation with the substitu-
tion of acidic hydrogen in the coordination link,in case of the
uranyl-ion,phosphoryl oxygen was found to take part in the coordina-
tion linkage.

The feasibility of uranyl nitrate extraction through both the
cation-exchange and solvation mechanisms is evidenced by the data
obtained by a number of ivestigators[19,20],the alternative of the
process course depending on the specific conditions.If the substitu-
tion of hydrogen ions and the coordination through phosphoryl oxygen
are observed simultaneously in the extraction process,then a chelate
is formed.

[x]The work by Yu.I.Vereschagin; V.S.Iliashenko, V.N.Kosiakov,
K.P.Lunichkina, L.A.Mamaev,V.G.Moskaliova,A.V.Strakhova is
used in this paper.

To evaluate the effect of the phosphororganic acid composition
and structure on the extraction power it is reasonable to study the
extraction of the elements and compounds known to react only through
one mechanism(e.g.nitric acid is extracted only through the solvation
mechanism while three-valent actinides and lanthanides-through the
cation-exchange one).

Extraction Mechanism

1.Nitric Acid Extraction. Nitric acid is extracted from solutions
simultaneously with cations or complexes and competes with them for
an extractant.

Therefore first of all the nitric acid extraction by phosphor-
organic acids was studied which differ in the radical length and struc-
ture,as well as in the number of the C-O-P links.

The quantitative characteristic of the nitric acid extraction is
given in table I.

As it follows from the cited results,the onset of the nitric acid
extraction occurs at its initial concentration of $\sim 4M$.

The dependence of the nitric acid distribution coefficient on the
HDEHP concentration as expressed in log-log scale,is described by the
equation of a straight line with a slope close to unity.This leads to
the conclusion that the monosolvate complex is formed.The nitric acid
extraction does not practically depend on the number of carbon atoms
in the RO-radical.However,the extractability of nitric acid is increas-
ed if an alkoxy radical is replaced by the CH_3-group,e.i.ethereal
oxygen is removed from an extractant molecule.This is in accordance
with the known line of increasing phosphororganic compound extraction

$$R_3PO > (RO)R_2'PO > (RO)_2R'PO > (RO)_3PO \qquad (21)$$
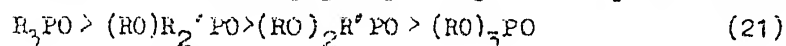
2.Extraction of U(VI).

Now a discussion will follow of our data on the extraction mechan-
ism of U(VI)from nitric and hydrochloric acid solutions.The mineral
acid concentration dependence of the distribution corfficients,shown
in fig.1,may be explained on the basis of the following considerations.

At low nitric acid concentrations the cation-exchange mechanism
is suitable for the uranium extraction(fig.2).It may be described by
the equation: $UO_2^{2+} + 2 H_2R_2 \rightleftharpoons UO_2(HR_2)_2 + 2H^+$ (3)

The increase Uextraction observed at the nitric acid concentration
above 3M is accounted for by the alteration of the extraction mechan-
ism.

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A rise of the nitric acid concentration is known to signifi-
cantly lower the dissociation degree of phosphororganic acids.Under
these conditions $(HNO_3 > 3M)$undissociated molecules of dialkyl-phos-
phoric acids start to show properties of neutral phosphororganic
reagents.In this case the following equation corresponds to the extrac-
tion mechanism:

$$UO_2^{2+}+2NO_3^-+2\ H_2R_2 \rightleftharpoons UO_2(NO_3)_2 \cdot 2H_2R_2 \qquad (4)$$
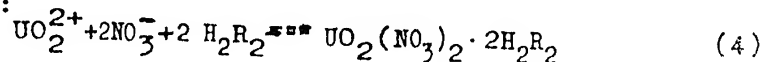
It is difficult to determine the strict range of nitric acid concentra-
tions over which one extraction mechanism is replaced by the other,as
there exists an acidity alteration range,within which both the cation-
exchange and the solvation are possible to act.

The maximum value of the distribution coefficient in the extrac-
tion by the solvation mechanism corresponds to the nitric acid concen-
tration of 5M.The subsequent lowering of U extraction is attributed
to the competitive behaviour of nitric acid.

Both the mechanisms,solvation and cation-exchange may be observed
separately on distributing slightly solvated uranyl-chloride between
the solutions of di-n-heptylphosphoric acid,tri-n-heptylphosphate and
aqueous hydrochloric acid solutions(fig.3).The extraction of uranyl
chloride by diheptylphosphoric acid is increased with the lowering of
nitric acid concentration and decreased in case of extraction by
triheptylphosphate.This corresponds to the cation-exchange and solvat
tion mechanisms,respectively.

To confirm these conclusions on the extraction nature of uranyl
nitrate,the infra-red absorption spectra were investigated of
$0.5M(n-C_7H_{15}O)_2POOH$ solution in CCl_4 before and after uranium extrac-
tion from the aqueous solutions containing 0.1, 0.5, 1.0, 2.0, 4.0,
6.0 and 8.0M nitric acid.For the sake of comparison similar
$(n-C_7H_{15}O)_3PO$ solutions in CCl_4were examined.The spectra of the
initial,$(n-C_7H_{15}O)_2POOH$ and $(n-C_7H_{15}O)_3PO$ solutions are most identi-
cal the principal difference of the $(n-C_7H_{15}O)_2POOH$ spectrum lying
in the presence of the bands in the $2300-2700cm^{-1}$region,characteristic
of the stretching vibrations of -OH,and the band at $\sim 1655cm^{-1}$ that
are likely to correspond to the bending vibrations of the same
group.The stretching vibration frequency of the P=O group for
$(n-C_7H_{15}O)_3PO$ is $1262cm^{-1}$(strong)and $1277cm^{-1}$(shoulder)and for
$(n-C_7H_{15}O)_2POOH$ is 1228^{-1}(strong);the stretching vibration of the

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(P)-O-C group is respectively,993cm^{-1}(shoulder),1016cm^{-1}(strong), 1050cm^{-1}(shoulder)and 1026cm^{-1}(strong),1063cm^{-1}(shoulder).

In the extraction by the$(n-C_7H_{15}O)_2POOH$ solution from 0.1M HNO$_3$ solutions the band P=O shifts up to 1200cm^{-1}(fig.4)and together with the principal band O-C,a shifted band 1070cm^{-1}appears approximately of the same intensity.Band at 937cm^{-1}also appears in the spectrum that corresponds to the antisymmetric valence vibration $\nu_3$of uranyl-group.

Similar changes are observed in case of the rest solutions as well until the nitric acid concentration in an aqueos solution becomes ~2M.On attaining this concentration and with its further rise the spectrum changes.The character of the band P=O is definitely changed. This band frequency is increased to 1210cm^{-1} while its intensity is secreased.Alongside this band another shifted one appeares and becomes more intense with the transition to stronger acidic solutions. The shifted band corresponds to stretching vibrations of more strongly bonded group P=O(1170cm^{-1}).The absorption band at 1255cm^{-1}that corresponds to the symmetric valence vibrations of NO$_2$and the band at 939cm^{-1}that corresponds to the antisymmetric valence vibrations ν_3 of uranyl group become more intense.

The O-C band shape is simplified and becomes similar to the shape of the band of the initial solution$(n-C_7H_{15}O)_2POOH$.

These results evidence to the fact that with the initial uranyl nitrate solution acidity increase from 2M and higher the extraction mechanism suffers changes which become more pronounced with the transition to high solution acidities.

We compared the absorption spectrum data with similar ones obtained for extraction of uranyl nitrate by$(n-C_7H_{15}O)_3PO$(fig.5). During extraction of uranyl-nitrate from 0.1 HNO$_3$aqueous solution alongside the principal doublet band P=O whose intensity decreases,a complex shifted band is observed with the maximum at 1185cm^{-1}.The intensity of this band grows with the increase of the nitric acid concentration to 0.5M.With a further acidity increase the intensity remains almost unaffected.The band shape gets gradually complicated due to the superposition of the additional bands of the nitrate group whose intensity insreased simultaneously with the increase of the band intensity at 939cm^{-1}(ν_3 of uranyl group).

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Thus,in case of uranyl nitrate extraction by$(n\text{-}C_7H_{15}O)_2POOH$
solutions from acid solutions(above 2M HNO_3)as well as in case of
extraction by$(n.C_7H_{15}O)_3PO$ solutions,the P=O stretching band shifting
to a lower frequency region is observed.It is indicative of the P=O
linkage weakening and of the participation of phosphoryl oxygen of
an extractant molecule in the formation of complexes being extracted.
The absorption bands of O-C(when forming complexes by the cited
extractants)suffered more complex changes,which are difficult to
compare,taking into consideration the difference in the structure of
the structure of the molecules themselves(frequency and character
changes in vibrations of groups $C_7H_{15}O\text{-}P$ in one case and $C_7H_{15}O\text{-}P$ and
HO-P groups in case of diheptyl phosphoric acid).

At the same time it is worth while mentioning that the absence
of more or less appreciable changes in the range of stretching vibra-
tions of OH^-in the spectra of solutions of uranyl complexes with
$(n\text{-}C_7H_{15}O)_2POOH$,in comparison with the spectrum of pure$(n\text{-}C_7H_{15}O)_2POOH$
is consistent with the results of Sato[19].However,an explanation offer-
ed by him- a new link formation with the hydrogen atom of HNO_3[22]resul-
ting in the appearance of a spectrum identical with the spectrum of
dimers of phosphororganic acids-appears to be doubtful.

Thus,infra-red spectrum data are an additional confirmation of the
existence of two different mechanisms of U extraction by phosphor-
organic acids:cation-exchange at low nitric acid concentration in
the aqueous phase and solvation at nitric acid concentration above 2M.

3.Extraction of Np(V) and Pu(IV)

The Np(V)behaviour was studied when extracting with solution
of di-(2-ethylhexyl)phosphoric acid(HDEHP)and mono-(2 ethylhexyl)phos-
phoric acid(H_2MEHP)in isooctane.Figs.6 and 7 show the distribution
coefficient of Np as a function of HNO_3concentration.

When analysing the results obtained it is necessary to take
into account the Np(V)instability.With the nitric acid concentration
above > 2M a marked disproportionation of Np(V) takes place.Therefore,
the extraction of Np(V)may be considered only in case of a solution
of low acidity.With the nitric acid concentration above 5M the dis-
proportionation effect is so high,that the obtained values of the
distribution coefficients refer to a mixture of four,five and six
valent ions of Np.The extraction of Pu(IV)was studied when extracting

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it from perchloric acid solutions with di-(2-ethylhexyl)phosphoric
acid in isooctane.

The results of the two series of the runs in which the dependence
of the distribution coefficients on the concentration of an extractant
and of hydrogen ions was determined(fig.8),lead to the conclusion that
the distribution coefficient is proportional to HDEHP concentration
to the second power and is inversely proportional to the H^+ concentra-
tion.Based on the dependences obtained the reaction may be represent-
ed by the following equation:

$$PuR_3^+ + 2Z_2R_2 \rightleftharpoons PuR_4 \cdot 3HR + H^+ \qquad (5)$$
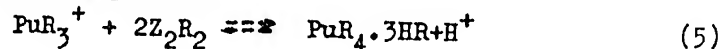
that is likely to be indicative of Pu(IV)complexing with di-(2ethyl-
hexyl)phosphoric acid in an aqueous phase.

As it can be seen from the results presented the extraction mechan-
ism of Np(V)and Pu(IV) has a complex nature.At the present time it
is imposible to strictly and simply express the interaction of these
elements with mono- and dialkyl phosphoric acids.Therefore,we confine
ourselves to the description of the mechanism(equation 5)resulting
from the discovered regularities neglecting the complex interactions
both in organic and in aqueous phases.

4.Extraction of Cesium

The mechanism of cesium interaction with di (2-ethyl hexyl)
phosphoric acid is defined from the study of the dependence of the
distribution coefficient on the concentration of extractant and
hydrogen ions.

The results of the experiments are shown in fig.9.The distribu-
tion coefficient of cesium is directly proportional to the square
of the HDEHP concentration and inversely proportional to the hydro-
gen ion concentration.From the data obtained the mechanism of cesium
extraction by di-(2-ethyl hexyl)phosphoric acid may be expressed by
the equation:

$$Cs + 2H_2R_2 \rightleftharpoons Cs(HR_2) \cdot H_2R_2 + H^+ \qquad (6)$$
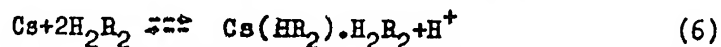
A similar mechanism was discovered for the extraction of sodium
by di-(2-ethylhexyl)phosphoric acid[18].

5.Extraction of Three Valent Elements

The distribution coefficients for americium,yttrium and cerium
in the extraction by HDEHP from nitric acid solutions diminish with
the nitric acid concentration rise(fig.6,10).

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In accordance with the obtained distribution coefficient
dependences on the extractant and hydrogen ion concentration the
extraction mechanism may be written in a general from:

$$Me^{3+}+3(H_2R_2) \rightleftharpoons Me(HR_2)_3+3H^+ \tag{7}$$
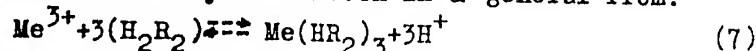
The equilibrium constant is expressed as

$$K= \frac{[Me\,(HR_2)_3][H^+]^3}{[Me^{3+}][H_2R_2]^3} \tag{8}$$

The complexing of these elements with mineral acid anions
being disregarded, equation(8) may assume the form:

$$\tilde{K} = Kp\, \frac{[H^3]}{[H_2R_2]^3} \tag{9}$$

To interpret the results the equilibrium constants $\tilde{K}$ are used,
obtained by extrapolation to the ion strength equal to 0. We do not
take into account the anion nature; because it was observed that the
nitrate - ion substitution by the chloride-ion in an aqueous phase
does not practically affect the distribution coefficient of americium,
cerium and europium (table II).

Similar results were obtained by Peppard[17] when extracting
curium and promethium from the nitric, hydrochloric and perchloric acid
solutions by $i(C_8H_{17}O)C_6H_5POOH$. The difference in the distribution
coefficients in the extraction from nitric and hydrochloric acid
solutions proved to be insignificant.

The same mechanism was observed in the extraction of americium
by mono-2-ethylhexyl phosphoric acid(fig. 11). However, in this case
the interpretation of the mechanism cannot be considered unequivocal
due to the complications that arise from the high polymerization
degree of mono-2-ethylhepyl phosphoric acid and requires further
refinement.

Effect of Phosphororganic Acid Structure and Composition
on Their Extraction Power
1. Effect of Radical Length

To examine the radical length effect of an organic compound on
its extraction power, dialkyl phosphoric acids in the range of
$(n-C_5H_{11}O)_2POOH$ to $(n-C_{12}H_{25}O)_2POOH$ with straight chain were used. The
extraction of plutonium and uranium was carried out with semi-molar
organic acid solutions from aqueous solutions, containing from 0.1 to
1.0M HNO_3. Americium was extracted from 0.1M nitric acid with 0.2M
extractants in toluene.

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The dependence of the distribution coefficient on the number of carbon groups is specific for various metals.This dependence is clear in the extraction of americium(fig.12),whose distribution coefficient increases sixfold with an increase of the number of carbon atoms from C_5 to C_{12}.In case of uranium and plutonium this dependence is less pronounced.It should be noted that the organic compound structure has a significantly stronger effect on the extraction of three valent actinides and lanthanides than on the extraction of such actinides as uranium or plutonium.This statement is also true of the concentration range of mineral acid whithin which only cation exchange mechanism is effective.

Fig.12 shows that the dependence of the distribution coefficient on the radical length also exists when the highly electronegative group-CH_2Cl is present in a molecule of an extractant.

2.Change of a Number of Oxygen Atoms

The extraction power of neitral extractants is significantly more affected by a change of a number of oxygen atoms than by any other changes of a compound structure[23,24].Thus,with the transition from phosphine oxide to phosphates the extraction power increases be more than 1000 times.

In the extraction with such acid compounds as R_2 POOH,R(RO)POOH, $(RO)_2$ POOH, RR_1POOH, $(RO)R_1$POOH, $R(R_1O)$POOH, where R is $1-C_8H_{17}$[x] and $R_1-C_6H_5$,the action is the same,but its influence is opposite(fig.13, 14),e.i.an increase in the number of oxygen atoms raises the extraction power.For example,with the transition from phosphinic acids $(1-C_8H_{17})_2$POOH and $(1-C_8H_{17})C_6H_5$ POOH when extracting americium and europium to phosphoric acids$(1-C_8H_{17}O)_2$POOH and$(1-C_8H_{17}O)C_6H_5O$ POOH the equilibrium constant is increased by 10^2 and 10^6,respectively.

The possible explanation of this fact may be found in the alteration of the electron density distribution when introducing electronegative groups and atoms.The introduction of an oxygen atom results in the electron density shift towards hydrocarbon radical which,in its turn,makes the oxygen of the oxygroup as if being more positive and leads to a higher mobility of hydroxyl hydrogen.

These conclusions correlate well with data[23]on the alteration of the extractant"acidity"as a function of a compound class.For

x) Here and below $1-C_8H_{17}$ is 2-ethylhexyl.

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example,pH of the semi-neutralization of di(2-ethyl-hexyl)phosphoric
acid is 3.2,while that of di(2-ethyl-hexyl)phosphinic acid is 5.6.It
is evident that,the difference in the pH value is accounted for by
the difference in the oxygen atom quantity in extractant molecule
of $\begin{smallmatrix}RO \\ R_1O\end{smallmatrix}$ POO type.In future it is supposed to examine whether this
effect is common for all the radicals in the extraction of a given
cation.

3.The aromatic radical effect on the equilibrium constant of Am
and Pm was tested by introducing an aromatic phenyl radical instead
of alkyl $R(i-C_8H_{17}-P)$into the molecule of an extractant of the
RR_1O POOH($i-C_8H_{17}O$ C_8H_{17}POOH) type.

As fig.15 shows,in the presence of phenyl group $i-C_8H_{17}O$ C_6H_5POOH
the equilibrium constant of Am and Pm is increased by two orders as
compared with the extractant containing radical with a normal chain.
The revealed effect is likely to be accounted for by an increase of
mobility of hydroxyl group hydrogen.

The introduction of chlorine instead of hydrogen into the CH_3^-
group of the $i-C_8H_{17}O$ CH_3 POOH molecule has a more pronounced effect
on the americium and promethium equilibrium constant(table III).

4.The octyl radical branching in the molecule,as it is shown
in figs.12,16, appreciably lowers the extraction of Am Pm,Pu(IV)
and U(VI).

The extraction of uranium and plutonium by di-(2-ethyl-hexyl)
phosphoric acid is reduced approximately by 6 times as compared to
the extraction by an extractant with normal octyl chains(fig.12).For
Am and Pu this effect is more significant(20 times)(fig.16).

A similar picture is observed when there is branching in benzene
ring(fig.15).When an octyl radical is replaced by a cyclic one the
equilibrium constant for Am and Pm is increased almost tenfold(fig.16)

Based on these data,an assumption is made to the effect that the
branching near a phosphorus atom shifts the "electron density"towards
hydroxyl,and thus lowers the organic acid dissociation.On the other
hand,the shielding of oxygroup hydrogen by the side chains is possible.

5)The diluent effect is pointed out in almost all the investiga-
tions into extraction(25,26).In case of neutral phosphororganic
compounds the diluent nature affects insignificantly the distribution
coefficients of the elements being extracted.Phosphororganic acids
are more sensitive to the diluent nature. When investigating the
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distribution of Am between 0.5M HNO_3 solution and 0.5M HDEHP solution in different diluents, the distribution coefficients were found to decrease by almost 100 times with the transition from isooctane to chloroform(table IV).The replacement of decane by toluene decreases the Am extraction by 100 times(table IV).

Dyrssen and Hardy[27] connect this effect with the degree of the extractant polymerization in an organic phase and with its interaction with a diluent.

As it is shown by a great number of authors[28], the dimerization is a principal form of monobasic acid association,but further molecule aggregation is most likely to take place due to dimer solvation by monomers.The solvation may be roughly characterized by the dielectric constant of a diluent.

These interactions are quantitatively estimated by Baes[29] from the product of the dimerization constant and the distribution coefficient of a monomer between organic and aqueous phases.For dibutyl-phosphoric acid this value amounts to 5.10^3.In fact,deviations from this value are observed effected in the first place, by the further aggregation of dimers and,in the second place,by the dissociation of the latter.The first interaction takes place in case of saturated hydrocarbons(kerosene)while the second one occurs in case of highly polar diluents(chloroform).When studying the extraction of Fe(III) with Di-(2-ethyl-hexyl)phosphoric acid in o octane,Dyrssen[30] discovered a partial trimerization of the extractant The further   polimeriza-
tion is particularly noticeable in the extraction of more highly charged cations.Chloroform solvates dimers rather intensely and preferentially through the hydrogen links.Thus,a molecule of a dimer is solvated by a polar diluent which makes it difficult for the cations being extracted to penetrate to the active centers of an extractant.Thus,when kerosene(the dielectric constant of 2.0) is replaced by chloroform(the dielectric constant of 5.1),the coefficient of uranium distribution between an aqueous solution and di-(2-ethyl-hexyl)phosphoric acid is almost 40 times decreased and that of americium is decreased by 1000times.It should be taken into account that the diluent influence greatly depends on the structure of the extractant itself.It follows from the above that the
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behaviour of the discussed elements in the extraction of phosphoric acids depends in a different way on the acidity of aqueous solutions, the diluent nature and complexing in an aqueous phase.All this makes it possible to design a variety of flow sheets for extraction, isolation, separation and refining of actinides and rare earths using alkyl phosphoric acids in combination with oxidation-reduction processes.

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Table 1

Nitric Acid Distribution

$(C_nH_{2n-1}O)_2$ POOH 0.3M in kerosene				$\begin{array}{c}CH_3 \\ C_nH_{2n-1}\end{array} \!\! P \!\! \begin{array}{c}O\\OH\end{array}$ 0.3M in kerosene		$(C_nH_{2n-1})_2$ POOH 0.3 M in toluene	
HNO_3 concentration	C_5	C_7	C_9	C_{12}	C_8	C_9	C_7	C_8
HNO_3 content in organic phase								
4M	0.023	0.02	0.023	0.023	0.096	0.058	0.098	0.107
6M	0.059	0.054	0.046	0.061	0.15	0.113	0.170	0.170
8M	0.095	0.112	0.110	0.111	0.21	0.174	0.231	0.240
10M	0.151	0.156	0.156	0.186	-	0.25	0.285	0.278

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Table II

Anion Effect on the distribution of Am, Ce, Eu

Extractant: $1\text{-}C_8H_{17}O \diagdown P \diagup O$ / $C_6H_5 \diagup \diagdown OH$ 0.1 M toluene

Acid concentration, M.		Am	Ce	Eu
0.05	HCl	9.7	6.55	108.0
	HNO$_3$	8.0	6.33	104.0
0.1	HCl	0.99	0.61	17.0
	HNO$_3$	0.74	0.45	14.0
0.2	HCl	0.08	0.054	1.78
	HNO$_3$	0.06	0.047	1.37
0.5	HCl	0.007	0.007	0.16
	HNO$_3$	0.006	0.005	0.065

Table III

Effect of Introduction of Radical Containing CCl on the Equilibrium Constant of Am and Pm.

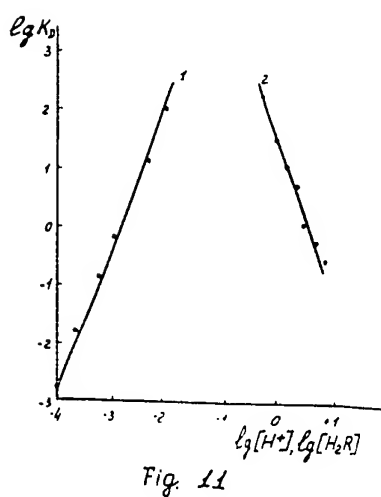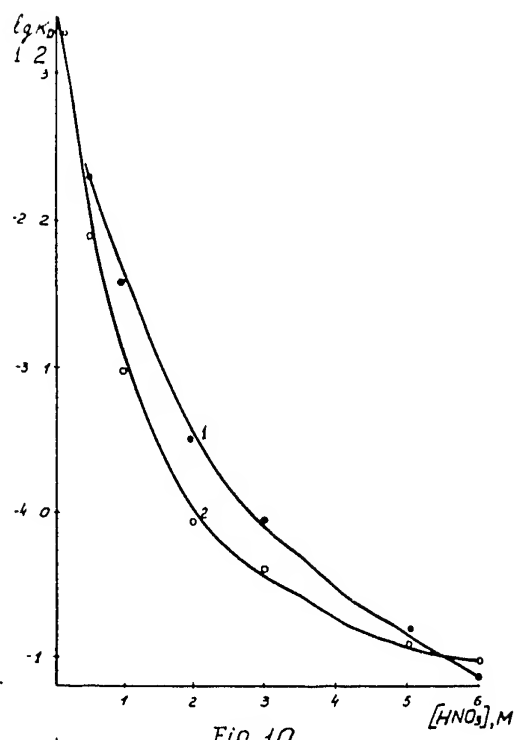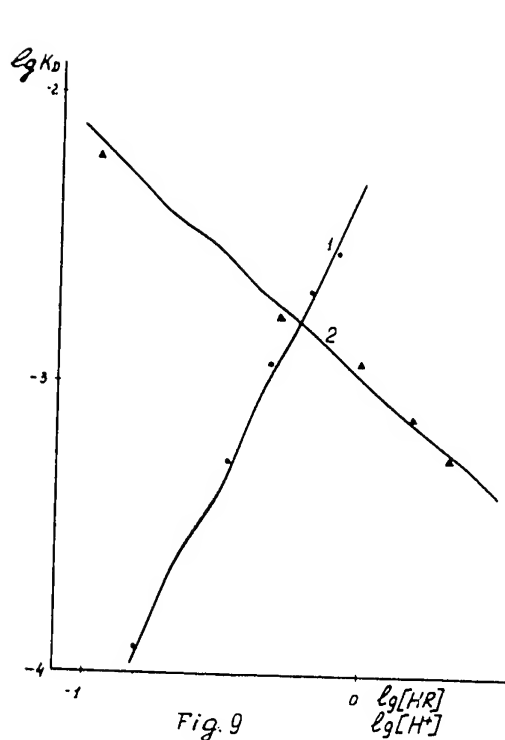| Extractant formula	$1\text{-}C_8H_{17}O \diagdown P \diagup O$ / $CH_3 \diagup \diagdown OH$	$1\text{-}C_8H_{17}O \diagdown P \diagup O$ / $CH_2Cl \diagup \diagdown OH$
K Am	0.1	8.8×10^3
K Pm	0.25	9.0×10^3

Table IV

Effect of Diluent Nature on Extraction of Am with HDEHP
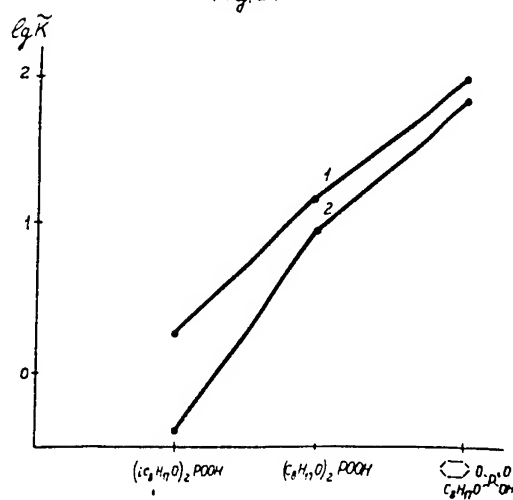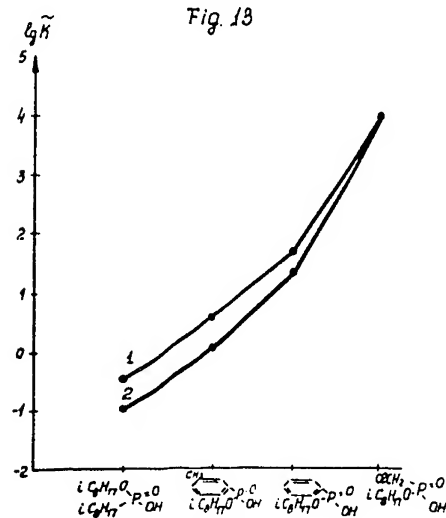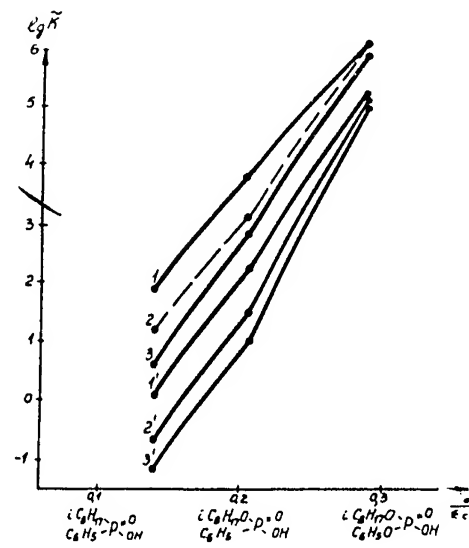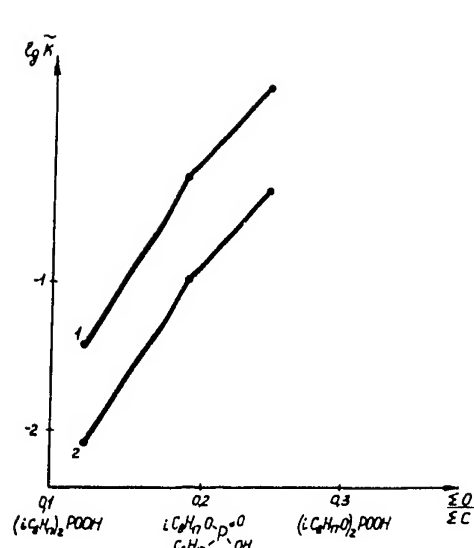
Aqueous Phase is 0.5M HNO_3

Diluent	Distribution coefficient
1. Isooctane	21.2
2. Decane	17.7
3. Cyclohexane	4.5
4. Carbon tetrachloride	0.49
5. Toluene	0.15
6. Benzene	0.092
7. Chloroform	0.0167

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Fig. 1

Fig. 2

Fig. 3

Fig. 4

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Fig. 5

Fig. 6

Fig. 7

Fig. 8

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Fig. 9

Fig. 10

Fig. 11

Fig. 12

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Fig. 13

Fig. 14

Fig. 15

Fig. 16

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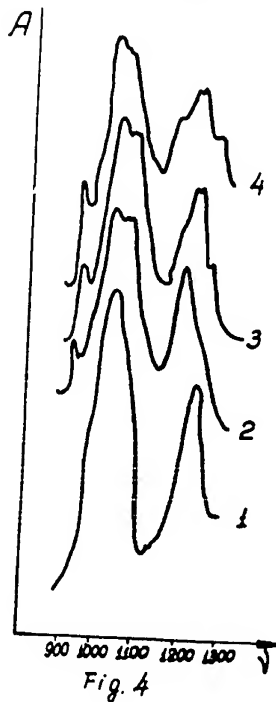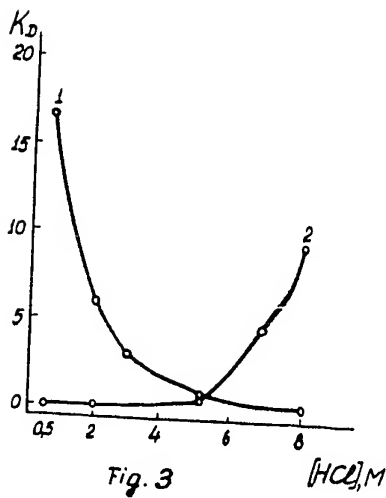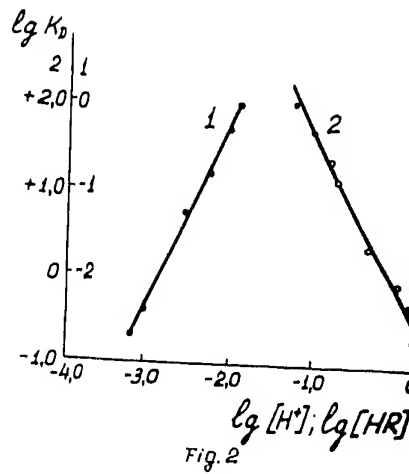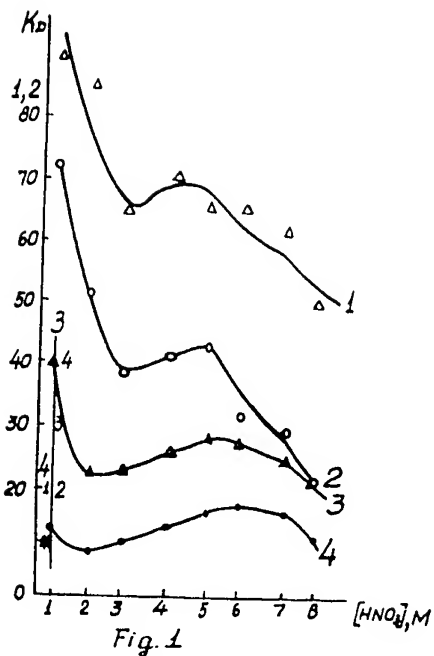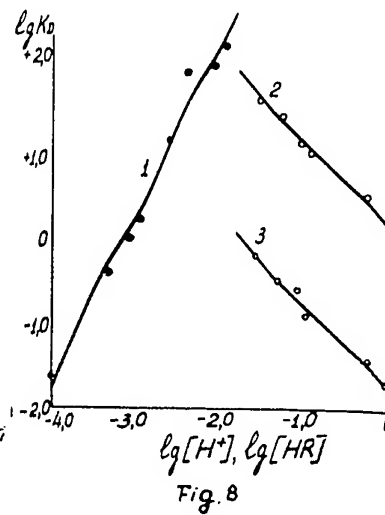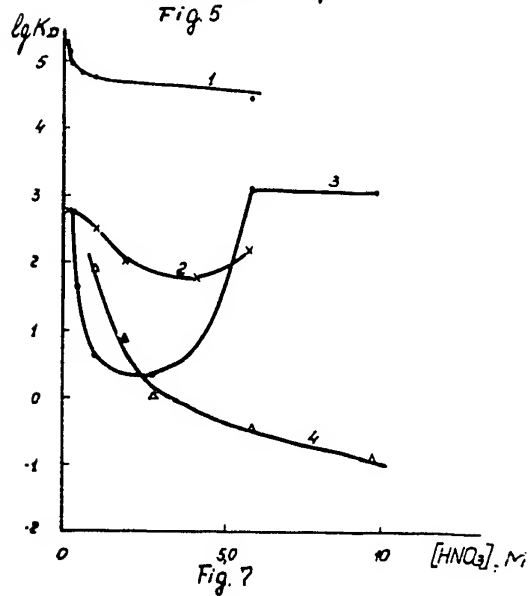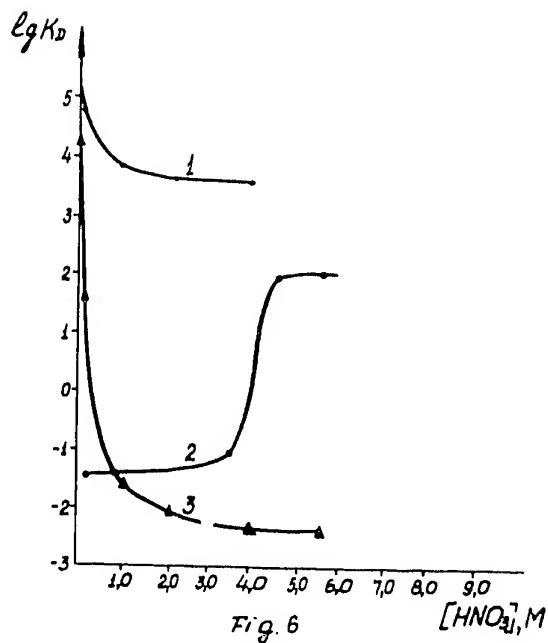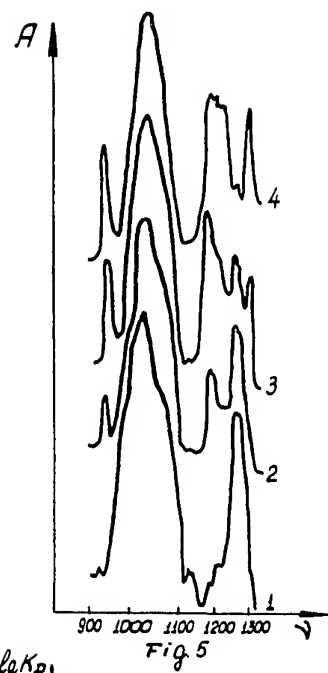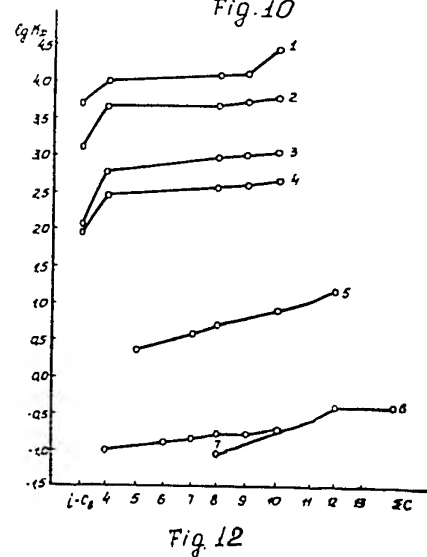
List of figures

Fig.1 Uranyl-nitrate distribution ratios as a function of HNO_3 concentration in aqueous phase and di-2-ethyl-hexyl phosphoric acid concentration in decane.

> 1.5% HDEHP
> 2.2,5%-"-
> 3.1,0%-"-
> 4.0,5%-"-

Fig.2 Extraction of U from perchloric acid solutions.

1. $[H^+]$ ion concentration - 1M

2. HDEHP concentration in isooctane - 0.005M.

Fig.3 Uranyl chloride distribution between 0.5M HCl and 0.5M solutions of $(C_7H_{15}O)_2POOH$ and $(C_7H_{15}O)_3PO$ in CCl_4.

Fig.4 Infra-red absorption spectra of solutions:

> 1) $(n-C_7H_{15}O)_2POOH$
> 2) $(n-C_7H_{15}O)_2POOH$ after uranyl nitrate extraction

from 0.1M nitric acid solution;

> 3) $(n-C_7H_{15}O)_2POOH$ after uranyl nitrate extraction

from 2.0M nitric acid solution;

> 4) $(n-C_7H_{15}O)_2POOH$ after uranyl nitrate extraction

from 8.0M nitric acid solution.

Fig.5 Infra-red absorption spectra of solutions:

> 1) $(n-C_7H_{15}O)_3 PO$;
> 2) $(n-C_7H_{15}O)_3 PO$ after uranyl nitrate extraction

from 0.1M nitric acid solution;

> 3) $(n-C_7H_{15}O)_3PO$ after uranyl nitrate extraction from

2.0M nitric acid solution;

> 4) $(n-C_7H_{15}O)_3PO$ after uranyl nitrate extraction from

8.0M nitric acid solution.

Fig.6 Distribution of actinides as a function of nitric acid concentration.Extractant 0.5M HDEHP.1.Pu; 2.Np; 3.Am.

Fig.7 Actinides distribution as a function of nitric acid concentration.Extractant 0.1M H_2MEHP.

> 1.Pu 2.U. 3.Np. 4.Am.

Fig.8 Extraction of Pu(IV)by HDEHP solutions in isooctane.
1. $[H^+]$ ion concentration-1M; 2.HDEHP concentration $-10^{-3}M$;
3.HDEHP concentration $- 10^{-4}M$.

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Fig.9 Extraction of Cs by HDEHP solution in decane.

1. $[H^+]$ ion concentration - 2M;

2. HDEHP concentration - 0.3M.

Fig.10 Extraction of Y and Ce from nitric acid solutions.

1. Ce, HDEHP concentration - 0.03M in kerosene.

2. Y, HDEHP concentration - 0.01M in kerosene.

Fig.11 Extraction of Am by H_2MEHP solution in decane.

1. $[H^+]$ ion concentration - 1,5M;

2. H_2MEHP concentration - 0.01M.

Fig.12 Distribution ratios of Am, Pu(IV) and U(VI) as a function of carbon atom number in the extractant radical(R).

1. Pu(IV); 0.1M HNO_3 ⎫
2. Pu(IV); 1.0M HNO_3 ⎪ 0.5M $(RO)_2PO(OH)$
3. U)VI); 0.1M HNO_3 ⎬ in isooctane.
4. U(VI); 1.0M HNO_3 ⎭

5. Am, 0.1M HNO_3-0.2M$(RO)_2PO(OH)$ ⎫ in
6. Am, 1.0M HNO_3-0.1M$(RO)(ClCH_2)$ ⎬ toluene
   PO (OH)

7. U(VI) 2.0M HNO_3-0.01M $R_2PO(OH)$ in xylene.

Fig.13 Effect of oxygen atoms on the equilibrium constant $(\tilde{K})$ Pm-1 and Am-2. Diluent:toluene.

Fig.14 Effect of oxygen atoms on the equilibrium constant $(\tilde{K})$. 1-Eu, 2-Pm, 3-Am in decane

2-Eu, 2-Pm, 3-Am in toluene.

Fig.15 Effect of electronegativity groops on the equilibrium constant in extraction. 1-Pm, 2-Am. Diluent:toluene

Fig.16. Effect of branched radicals on the equilibrium constant $(\tilde{K})$. 1-Pm, 2-Am.

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